EPR Investigation into the Kinetics and Mechanism of the One-electron Reduction of Benzenediazonium Ions by Fe^{II}–EDTA and other Iron(II) complexes

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An EPR approach has been developed and applied to the determination of the rate constants for the decomposition of some arenediazonium ions by Fe^{II} complexes to give aryl radicals. In continuous-flow experiments, steady-state concentrations have been measured both for the aryl radical-adducts to the fumarate anion and for $^{\bullet}CH_2CO_2^-$ (obtained by reaction of $Ar^{\bullet}$ with the iodoacetate anion): analysis of the dependence of these upon $[Fe^{II}]$ and $[ArN_2^+]$ leads to values of the rate constants for electron transfer.

For the reaction between Fe^{II}–EDTA and a series of diazonium ions, for which values of k are in the range 2×10^4–4×10^5 dm^3 mol^{-1} s^{-1}, it is shown that there is a good dual-parameter Hammett–Taft correlation (involving σ_I and σ_R^+, and with $\rho = 1.74$), consistent with the occurrence of an outer-sphere electron-transfer process.

There is a considerable contemporary interest both in the mechanisms of single-electron transfer reactions (including those which lead to the formation of organic free radicals)[1] and in the effectiveness with which free radicals can be employed in synthesis.[2] These two features are common to the formation and reactions of aryl radicals generated by one-electron reduction of the corresponding diazonium ions, as in the well-known Sandmeyer and Gatterman synthetic procedures (and recently reviewed by Galli[3]).

We have been particularly interested in using the technique of EPR spectroscopy to explore directly the factors which control the homolytic decomposition of peroxides and other substrates *via* one-electron transfer from low-valent transition-metal ions. For example, the mechanistic contrasts between the reactions between Fe^{II} and Cu^{I} with, *e.g.* $HOOSO_3^-$, have recently been revealed [see reactions (1) and (2)[4,5]] and clear distinctions made between the occurrence of inner-sphere and outer-sphere electron-transfer processes (with *e.g.* H_2O_2 and $S_2O_8^{2-}$, respectively). As a continuation of our related interest in the rates and mechanisms of reaction of transition-metal ions with diazonium ions[6] we have now extended our EPR spectroscopic and kinetic analysis in order to obtain evidence that reaction (3) proceeds effectively through a single-electron transfer process, to give free radicals, and to obtain relevant kinetic information.

$$\mathrm{Fe^{II} + HOOSO_3^- \longrightarrow Fe^{III} + HO^- + SO_4^{\bullet -}} \tag{1}$$

$$\mathrm{Cu^{I} + HOOSO_3^- \longrightarrow Cu^{II} + HO^{\bullet} + SO_4^{2-}} \tag{2}$$

$$\mathrm{Fe^{II} + ArN_2^+ \longrightarrow Fe^{III} + ArN_2^{\bullet} \longrightarrow Ar^{\bullet} + N_2} \tag{3}$$

Results and Discussion

Development of an EPR Method Suitable for Kinetic Analysis.—We have previously described[7] the use of a rapid-mixing three-way flow system in conjunction with an EPR spectrometer to study the generation and reactions of the phenyl radical, formed by the reaction of Ti^{III}–EDTA† and $C_6H_5N_2^+$ in aqueous solution at pH *ca.* 8. An excess of maleic acid or iodoacetic acid was used to scavenge aryl radicals produced during the reaction (*via* addition to the double bond in the former, *via* iodine abstraction in the latter) and EPR spectroscopy employed to verify the occurrence of reactions (4) and (5) or (6), and to determine the steady-state concentration of the resulting radicals. Kinetic analysis, achieved *via* study of the dependence of, for example, the concentration of **1** on $[Ti^{III}]_0$ $(=[ArN_2^+]_0)$, was used to calculate the rate constant for reaction (4) in aqueous solution at room temperature [$(1.9 \pm 0.3) \times 10^3$ dm^3 mol^{-1} s^{-1}].

$$\mathrm{Ti^{III} + ArN_2^+ \longrightarrow Ti^{IV} + Ar^{\bullet} + N_2} \tag{4}$$

$$\mathrm{Ar^{\bullet} + {}^-O_2CCH{=}CHCO_2^- \longrightarrow \underset{\textbf{1}}{{}^-O_2C(Ar)CH\text{–}\dot{C}HCO_2^-}} \tag{5}$$

$$\mathrm{Ar^{\bullet} + ICH_2CO_2^- \longrightarrow ArI + {}^{\bullet}CH_2CO_2^-} \tag{6}$$

Fe^{II}–EDTA was chosen for initial study here, rather than $Fe^{II}(H_2O)_6$, since the former has a lower redox potential $[E^{\circ}(Fe^{3+}/Fe^{2+}) = 0.12\ \mathrm{V}]$, similar to that of aqueous copper(I), so that rapid reactions to give free radicals might be anticipated.[8] The experimental arrangement for EPR studies typically involved the mixing of three deoxygenated aqueous solutions *ca.* 35 ms before passage through the cavity of the spectrometer. The solutions normally contained Fe^{II} [iron(II) sulfate, together with the sodium salt of EDTA in a twofold molar excess], the appropriate arenediazonium tetrafluoroborate (with concentrations after mixing of these reagents typically in the range 0.5–5.0 × 10^{-3} mol dm^{-3}), and the scavenging agent (usually fumaric acid, but in some cases iodoacetic acid, typically at a final concentration of *ca.* 0.1 mol dm^{-3}). The pH of the mixed solution was adjusted to *ca.* 9 by the addition of ammonia solution to the third stream.

Continuous-flow experiments were carried out involving a series of arenediazonium ions (ArN_2^+; Ar = 4-C_6H_4X; X = H, OMe, Me, F, Cl, CO_2Et, NO_2, NMe_2), with concentrations of the diazonium ion and Fe^{II}–EDTA typically 10^{-3} mol dm^{-3} (after mixing). For the first five substrates, strong signals were detected from the appropriate adduct **1** of fumaric acid, with a(α-H) = 2.04 and a(β-H) = 1.07 mT, g = 2.0033, and from $^{\bullet}CH_2CO_2^-$, with a(α-H) = 2.12 mT, g = 2.0032, from iodoacetic acid (see Fig. 1). The signals from the adducts **1** were

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† EDTA = Ethylenediaminetetraacetic acid

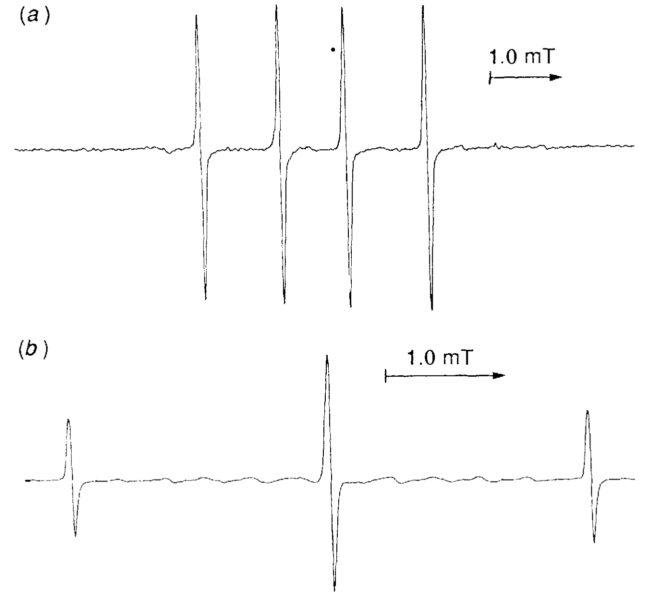

Fig. 1 (*a*) EPR spectrum of the phenyl radical-adduct to fumaric acid, obtained from a continuous-flow EPR study of the reaction between Fe^{II}-EDTA and $C_6H_5N_2^+$ (both 2.66×10^{-3} mol dm^{-3}) in the presence of fumaric acid (0.12 mol dm^{-3}) at pH 9. (*b*) EPR spectrum of the radical $^\bullet CH_2CO_2^-$ obtained from a continuous-flow EPR study of the reaction of iodoacetic acid (0.072 mol dm^{-3}) with the phenyl radical, generated from the reaction between Fe^{II}-EDTA and $C_6H_5N_2^+$ (both 2.66×10^{-3} mol dm^{-3}) at pH 9.

particularly intense, an observation which presumably reflects the effect of the double negative charge in lowering the rate constant for radical termination (expected to be *ca.* 1×10^7 dm^3 mol^{-1} s^{-1}; *cf.* ref. 9); in contrast, $2k_t$ for $^\bullet CH_2CO_2^-$ is reported as 1×10^9 dm^3 mol^{-1} s^{-1}.[10] [For this reason fumaric acid was generally employed as the reagent for scavenging (trapping) aryl radicals and for obtaining kinetic information.] In contrast, only very weak signals were obtained for the arenediazonium ions with nitro and ethoxycarbonyl substituents, and no signals at all could be detected from the dimethylamino-substituted analogue.

Preliminary experiments were conducted (for the unsubstituted diazonium ion itself and the substituted analogues which gave good signals) in which the steady-state concentrations of adducts $R^\bullet$ (*i.e.* **1**) were monitored as a function of the initial (equimolar) concentrations of ArN_2^+ and Fe^{II}-EDTA. Under these conditions, and on the assumption that following their generation *via* reactions (3) and (5) the radical-adducts simply react *via* bimolecular termination (with rate constant $2k_t$) it can be shown[7] [eqn. (7)] that the following analytical solution can be obtained for the radical-adduct's concentration at a time t after mixing.

$$[R^\bullet]^{-1} = (2k_t/k_3)^{\frac{1}{2}}([Fe^{II}]_0^{-1} + k_3 t) \qquad (7)$$

This analysis was previously successfully employed for a study of the corresponding reaction between Ti^{III} and $C_6H_5N_2^+$:[7] by obtaining values of $[R^\bullet]$ at varying $[Ti^{III}]_0$ ($=[ArN_2^+]_0$) and plotting $[Ti^{III}]_0^{-1}$ *vs.* $[R^\bullet]$ values for k_4 and $2k_t$ were calculated from the gradient and intercept.

Results for the Fe^{II}–EDTA/ArN_2^+ redox couples plotted according to eqn. (7) gave a series of linear variations, as predicted, but the relatively large errors on the (small) intercept on the $[R^\bullet]^{-1}$ axis imply that reliable values of $2k_t$ and k_3 cannot be obtained in this way. For example, calculated values of $2k_t$ varied between 5×10^6 and 10^8 dm^3 mol^{-1} s^{-1}, which would not have been anticipated since the 4-substituent in the ring would not be expected to perturb to that extent the value of the termination rate constant $2k_t$ for the adducts (see later).*

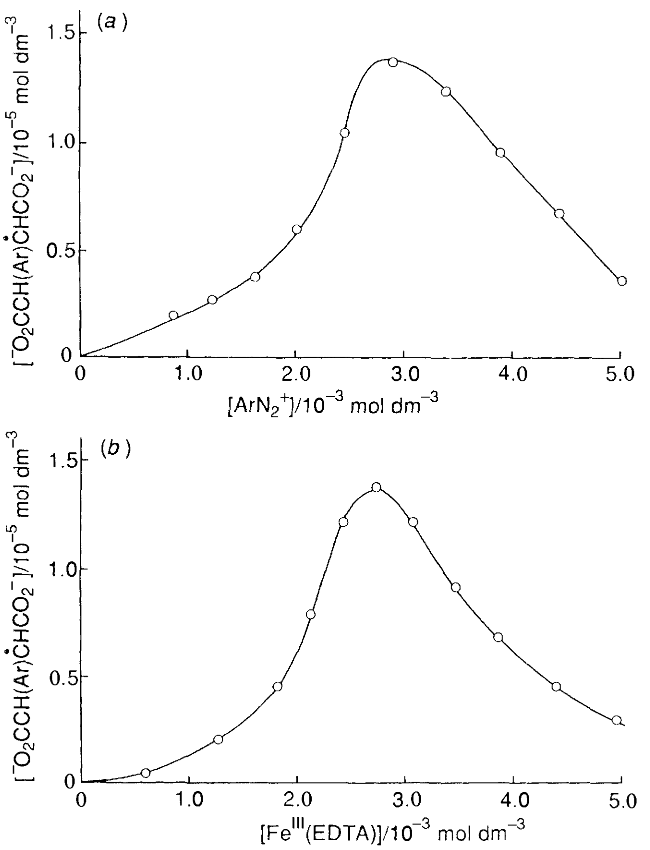

Fig. 2 (*a*) Variation in the steady-state concentration of the phenyl-radical adduct of fumaric acid, generated in a continuous flow system with the concentration after mixing of $C_6H_5N_2^+$ (with $[Fe^{II}$-EDTA$]$ = 2.66×10^{-3} mol dm^{-3}, [fumaric acid] = 0.12 mol dm^{-3}, pH 9; time between mixing and detection 0.035 s). (*b*) Variation in the steady-state concentration of the phenyl-radical adduct of fumaric acid, generated in a continuous flow system, and detected by EPR, with the concentration after mixing of Fe^{II}-EDTA (with $[C_6H_5N_2^+]$ = 2.66×10^{-3} mol dm^{-3}, [fumaric acid] = 0.12 mol dm^{-3}, pH 9; time between mixing and detection 0.035 s).

Instead, we explored the possibility of employing computer simulation of kinetic EPR results (applicable to conditions other than those in which initial reagent concentrations are equal) to determine more accurate values for k_3 for a variety of different arenediazonium ions, for which relatively small differences might be expected. Use of the computer program has been previously described.[4,5]

Kinetic Analysis of the Fe^{II}–EDTA/ArN_2^+ *Reaction* via *Kinetic Simulation*.—We first explored the observed variation in $[R^\bullet]$ (*i.e.* [**1**]) when the initial concentration of one reagent was varied, with the other being held constant. Fig. 2(*a*) shows a typical set of results, obtained from the addition of $Ph^\bullet$ (from the benzenediazonium ion) to fumaric acid, in experiments with Fe^{II}–EDTA (initial concentration 2.66×10^{-3} mol dm^{-3}) and benzenediazonium tetrafluoroborate [with initial concentrations after mixing in the range (0.87–5.58) $\times$ 10^{-3} mol dm^{-3}]. As can be seen, a clearly defined maximum in the radical-adduct concentration is observed; the maximum appears to occur at a concentration of the diazonium ion equal

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* This should certainly be true for the appropriate dimerization reaction, though disproportionation, and the ratio of dimerization to disproportionation, might well be sensitive to substituent effects (*via* effects on the C–H bond dissociation energy).

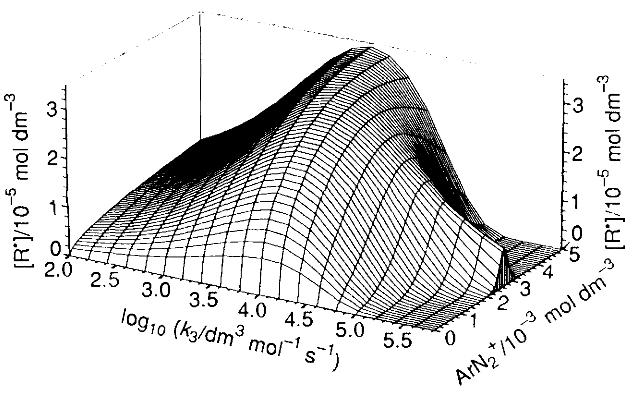

Fig. 3 Simulations of concentrations of the phenyl-radical adduct of fumaric acid for the reaction of Fe^{II}–EDTA, $C_6H_5N_2^+$ (the concentration of one of which was varied), and fumaric acid, using the reaction scheme given by eqns. (3) and (5) and with bimolecular self-termination, for different values of k_3 (other conditions as in Fig. 2).

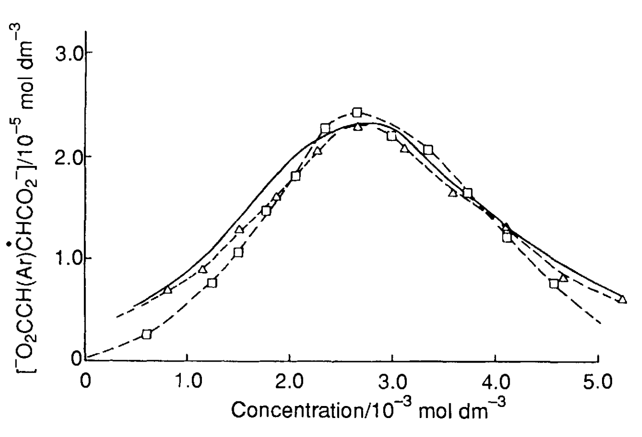

Fig. 4 Variation in the concentration of $^{\bullet}CH_2CO_2^-$ (generated in a steady-state concentration in continuous flow experiments) with the concentration after mixing of Fe^{II}–EDTA (□) or $C_6H_5N_2^+$ (△), the other concentration being held constant (2.66×10^{-3}); with [iodoacetic acid] = 0.072 mol dm^{-3}, pH 9, and time between mixing and observation 0.035 s. The concentrations calculated with a value of $k_3 = 1.6 \times 10^5$ dm^3 mol^{-1} s^{-1} are also shown (——).

to that of the metal ion. Similar results were obtained when the experiment was conducted for fixed $[C_6H_5N_2^+]_0$ and varying [Fe^{II}–EDTA]$_0$ [see Fig. 2(*b*)]. A kinetic analysis which shows that a maximum in [R•] should occur for equal concentrations of reagents for a certain range of reduction rate constants is given in the Appendix.*

Using the kinetic simulation program described earlier, we also explored the predicted behaviour of this system by calculating the expected radical concentration as a function of $[ArN_2^+]_0$ for a given concentration of [Fe^{II}–EDTA]$_0$, for a variety of values of k_3 (the rate constant for the initiation reaction); other input parameters were as follows: t (mixing time) = 0.035 s, $k_5 = 1 \times 10^6$ dm^3 mol^{-1} s^{-1} [there is no specific precedent quoted in the literature for this reaction (but see ref. 7), but for the concentrations of radical scavengers employed the calculations were insensitive to its variation], and $2k_t = 10^7$ dm^3 mol^{-1} s^{-1} (see earlier). Fig. 3 shows the three-dimensional representation of the results, plotted as calculated

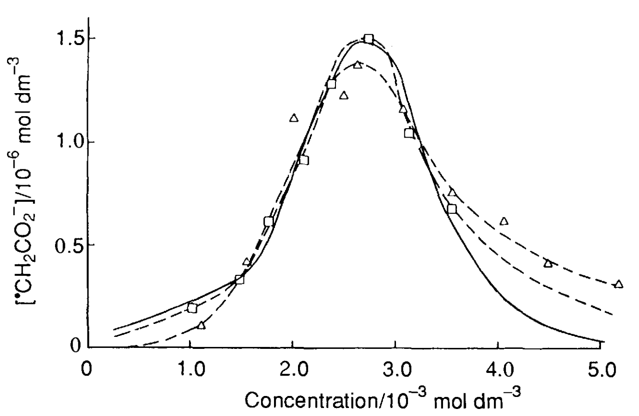

Fig. 5 Variation in the concentration of the 4-methylphenyl radical-adduct of fumaric acid formed in the reaction between Fe^{II}–EDTA and $4\text{-}MeC_6H_4N_2^+$, as a function of Fe^{II}–EDTA (□) and ArN_2^+ (△) (the other concentration being held constant at 2.66×10^{-3}); with [fumaric acid] = 0.12 mol dm^{-3}, pH 9 and time between mixing and observation of 0.035 s. The concentrations calculated with values of $k_3 = 8.0 \times 10^4$ dm^3 mol^{-1} s^{-1} and $2k_t = 8.0 \times 10^6$ dm^3 mol^{-1} s^{-1} are also shown (——).

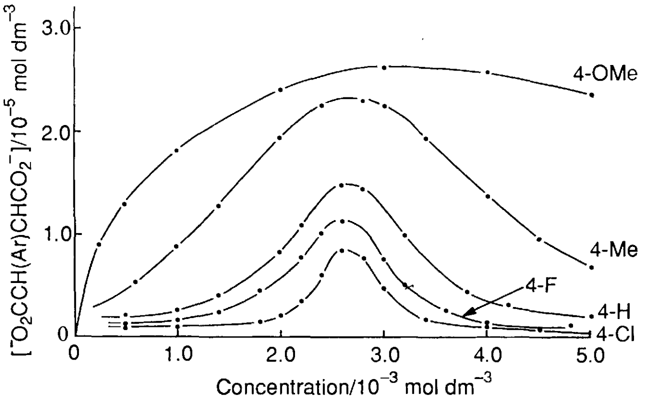

Fig. 6 Variation in the calculated concentrations of aryl-radical adducts of fumaric acid as a function of $[ArN_2^+]$ or [Fe^{II}–EDTA] for different 4-substituents in the aryl ring: the curves shown are those which provide optimum fitting for experimental results

values of [R•] as a function of $[ArN_2^+]$ (or [Fe^{II}–EDTA]) and $\log_{10} k_3$. As can be seen, for values of k_3 in the range *ca.* 5×10^4–*ca.* 10^6 dm^3 mol^{-1} s^{-1} the prediction of a well-defined maximum in [R•], with $[ArN_2^+]$ = [Fe^{II}–EDTA], clearly matches the experimental results shown in Fig. 2 (and the analysis given in the Appendix). As k_3 is progressively reduced, it is predicted first that the maximum rises in value, with a less steep slope either side, with a subsequent shift in the maximum to higher $[ArN_2^+]$ (*e.g.* for $k_3 <$ *ca.* 5×10^3); ultimately, for much lower values of k_3 (< *ca.* 10^2 dm^3 mol^{-1} s^{-1}), the predicted steady-state radical concentrations drop (*i.e.* radicals are not being generated sufficiently rapidly for detection of a strong signal).

Values of k_3 were then derived by computer-fitting of experimental results for each of the series of diazonium ions—in each case for sets of experiments in which concentrations of both reagents were separately varied (the other being held constant). As expected more or less identical behaviour was obtained for variation of either $[ArN_2^+]_0$ or [Fe^{II}–EDTA]$_0$. This observation rules out participation of reactions of the intermediate aryl radicals or radical-adducts with either of the starting materials under the conditions employed (*e.g. via* radical reduction with Fe^{II} or addition to parent diazonium ion, for which precedents exist[11,12]). In fitting results, attention was paid not only to the height of the maximum (*i.e.* the predicted

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* The occurrence of such a maximum is perhaps not surprising, at least from a qualitative viewpoint. For low values of the variable concentration, the reduced value of the steady state concentration $[R^{\bullet}]_{SS}$ simply reflects the low rate of the initiation reaction; for very high values of the reactant concentration, the subsequent rapid reaction will lead to a significant depletion of reagent concentrations before the cavity is reached.

Table 1 Rate constants for the one-electron reduction of arenediazonium ions 4-X-$C_6H_4N_2^+$ by Fe^{II}–EDTA[a,b]

X	k_3/dm^3 mol^{-1} s^{-1}	$2k_t$/dm^3 mol^{-1} s^{-1} [c]
OMe	2.2×10^4	1.5×10^7
Me	8.0×10^4	8.0×10^6
H	1.8×10^5	1.0×10^7
F	2.5×10^5	1.5×10^7
Cl	3.8×10^5	1.7×10^7

[a] In aqueous solution (pH 9) at room temperature. [b] Errors in the calculated value of k_3 are estimated to be ±10%. [c] Values of $2k_t$ for the aryl adducts of fumarate, **1**, which give optimum agreement between calculated and experimental dependence of [**1**] on [ArN_2^+] and [Fe^{II}–EDTA] (see the text).

Table 2 Steady-state concentrations of phenyl-radical adducts of fumarate anion as a function of added ligand in continuous-flow EPR experiments involving Fe^{II}–L and $C_6H_5N_2^+$ [a]

Ligand (L)[b]	E° (for Fe^{III}/Fe^{II} for complex)/V[c]	[R$^\bullet$]/10^{-5} mol dm^{-3}
H_2O	0.77[d]	—
CN^-	0.36[e]	—
NTA	0.33[f]	0.13
citrate	0.33[g]	1.46
tartrate	—	1.29
EDTA	0.12[d]	1.51
HEDTA	0.11[d]	1.99

[a] In experiments at pH 9 with $[C_6H_5N_2^+]_0 = [Fe^{II}] = 2.66 \times 10^{-3}$ mol dm^{-3}, [fumarate] = 0.12 mol dm^{-3}, with time between mixing and observation *ca.* 0.035 s. [b] Two moles of complexing agent employed per mole of Fe^{II} except for H_2O and CN^-. [c] E° measured with respect to the normal hydrogen electrode. [d] Ref. 8. [e] Ref. 17. [f] G. Swarzenbach and J. Heller, *Helv. Chim. Acta*, 1951, **34**, 1889. [g] R. E. Hamm, C. A. Shull and D. M. Grant, *J. Am. Chem. Soc.*, 1954, **76**, 2111.

maximum radical concentration) but also the shape of the experimental curves.

The data obtained for $C_6H_5N_2^+$ were satisfactorily simulated with a rate constant for radical initiation (Fe^{II}–EDTA/$C_6H_5N_2^+$) of 1.8×10^5 dm^3 mol^{-1} s^{-1} (with $2k_t = 1 \times 10^7$ dm^3 mol^{-1} s^{-1}). To verify the appropriateness of our kinetic analysis and calculated value, we repeated this experiment with ICH_2CO_2H as radical scavenger (see Fig. 4). As shown in the Figure there is good agreement (with the height and shape of the maximum in the curve) between experimental results and those calculated using $k_3 = 1.6 \times 10^5$ dm^3 mol^{-1} s^{-1}, $k_6 = 1.0 \times 10^6$ dm^3 mol^{-1} s^{-1} and $2k_t$ (for $^\bullet CH_2CO_2^-$) $= 1 \times 10^9$ dm^3 mol^{-1} s^{-1}. Fig. 5 shows the experimental and calculated results for the formation and trapping of the 4-methylphenyl radical in the fumaric acid system: optimum agreement was obtained for an initiation rate constant of 8.0×10^4 dm^3 mol^{-1} s^{-1} and a slightly different termination rate constant of 8×10^6 dm^3 mol^{-1} s^{-1}.

Satisfactory results were obtained in this way for the diazonium ions ArN_2^+; Ar = 4-C_6H_4X; X = H, OMe, Me, F, Cl. For these substrates rate constants are summarized in Table 1 (*n.b.* Fig. 6 illustrates the sensitivity of the method to variation in k_3). There is a small but significant increase in k_3 as the electron-withdrawing nature of the substituent is increased; the optimum calculated values of $2k_t$ vary only slightly with X (as might have been expected).

In view of these results, it seems likely that for the diazonium ions with the electron-withdrawing groups CO_2Et and NO_2 as 4-substituent the weakness of the signals obtained reflects the relative rapidity of the initial electron transfer reaction (*i.e.*, $k_3 > 10^6$ dm^3 mol^{-1} s^{-1}). Failure to detect signals from 4-$Me_2NC_6H_4N_2^+$ may reflect either a significant retardation in the initiation reaction and/or the rapid reaction between Ar$^\bullet$ and the parent diazonium ion in this case (see *e.g.* ref. 12, 13).

Complexation of Iron(II) *with Other Ligands*.—An experimental approach similar to that described above was adopted to explore the effect of variation in the ligand used to complex Fe^{II}. Most of the experiments were carried out with the unsubstituted diazonium ion itself: the concentration of the phenyl adduct of fumarate was then monitored as a function of ligand under conditions where equimolar concentrations of diazonium ion and metal complex were employed (each 2.66×10^{-3} mol dm^{-3}).

Under these conditions no EPR signals could be obtained from reaction of Fe^{II}_{aq} or $Fe(CN)_6^{4-}$ with $C_6H_5N_2^+$, and we suggest that in these cases the reaction rate constant is too low (< *ca.* 10^3 dm^3 mol^{-1} s^{-1}) for sufficient radicals to be generated in the cavity; in view of the relatively high values of E° for these complexes (see Table 2) compared with the EDTA complex this is perhaps not unexpected. Weak signals of the appropriate adduct were detected in the reaction of $Fe(CN)_6^{4-}$ with 4-$O_2NC_6H_4N_2^+$, which may well reflect an enhancement in rate constant as a result of the expected greater ability of this 4-substituted diazonium ion to act as an oxidant compared with the unsubstituted ion.

EPR signals were obtained from the unsubstituted diazonium ion in experiments with added ligands as given in Table 2 (which also contains the reduction potentials of the appropriate iron complexes, where these are known). The signals detected in experiments with iron(II) complexes ligated by HEDTA,* citrate and tartrate were found to be similar in magnitude to those observed for EDTA under identical conditions, which is broadly as expected if the rate of reaction is governed largely by the reduction potential of the metal complex. A very weak signal was detected from Fe^{II}–NTA,† which may reflect the relatively high value of E° for this ligand compared with EDTA (and hence an anticipated reduction in the rate constant). Our finding that an increased signal of the appropriate adduct was detectable in identical experiments with Fe^{II}–NTA and the 4-nitro-substituted benzenediazonium ion (which would be expected to undergo electron transfer more rapidly than the unsubstituted ion) appears to support this explanation.

Interpretation of Results.—For the reactions of the series of diazonium ions with Fe^{II}–EDTA a plot of log (k_3^X/k_3^H) *versus* Hammett's σ values is curved, and a wide scatter ($100R^2$ = 96.2) resulted for a similar plot against σ^+.[14] However, correlation using Taft's bisected substituent constants (σ_I and σ_R^+) does give a linear plot (Fig. 7) for which the correlation expression is given by eqn. (8).[15] Taft's other σ_R scales [$\sigma_{R(BA)}$, σ_R^0, σ_R^-] all gave poorer correlations.

$$\log (k_3^X/k_3^H) = (1.74 \pm 0.08)[\sigma_I + (0.78 \pm 0.06)\sigma_R^+] = \rho(\sigma_I + \lambda\sigma_R^+) = \rho\bar{\sigma} \quad (8)$$
$$[100R^2 = 99.7, F = 344.1; F_{99.0} = 99.0]$$

The positive reaction constant (1.74) reflects the observation that the reaction is facilitated by electron-withdrawal in the diazonium ion, as expected for rate-determining electron transfer to this species. In the diazonium ions $+M$ substituents conjugate directly with cationic charge (see **2a** and **2b**); such conjugation should persist in the transition state for outer-sphere electron transfer since the reactant orbitals will not be strongly perturbed (see *e.g.* ref. 1).

The findings that the Hammett–Taft correlation implicates σ_R^+ is consistent with conjugation between the substituent and

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* HEDTA = *N*-(2-Hydroxyethyl)ethylenediaminetetraacetic acid.

† NTA = Nitrilotriacetic acid.

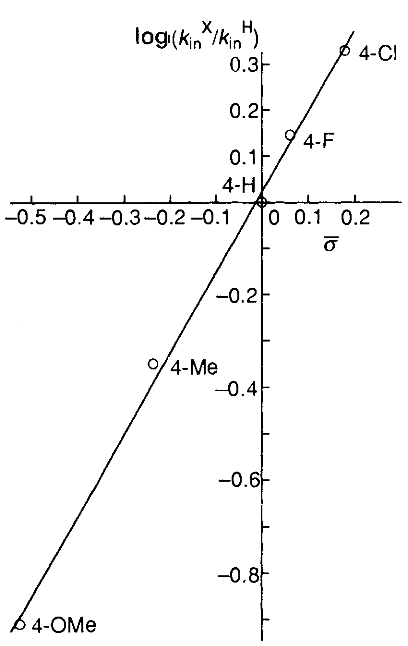


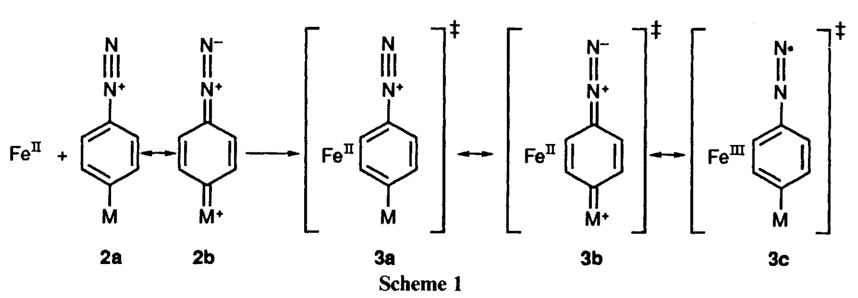
Fig. 7 Dual-parameter Hammett plot showing the linear relationship between the logarithm of the relative values of the rate constants for reduction of arenediazonium salts with Fe^{II}–EDTA and the optimum combination of Taft's values of σ_I and σ_R^+. [$\bar{\sigma} = (\sigma_I + 0.78\sigma_R^+)$]

cationic charge in the transition state, although the extent of this is reduced relative to the reaction which defines σ^+ and hence σ_R^+ (hydrolysis of cumyl chlorides[14,15]) as shown by the value of λ ($0.78 < 1$). It is generally agreed that the transition state for hydrolysis of cumyl chlorides closely resembles the cumyl cation, thus the present observation of $\lambda = 0.78$ would be consistent with an electron–transfer transition state **3** in which contribution from the charge-transferred canonical form **3c** is significant.

The present results may be compared with others for the reductions of diazonium ions by different Fe^{II} complexes (Table 3). Doyle[16] reported kinetics of the reduction of diazonium ions by aqueous ferrocyanide and by decamethylferrocene in MeCN, both reagents being chosen as characteristic outer-sphere electron–transfer reductants; he found that Hammett correlations of his data were best made using σ rather than σ^+.

We have subjected Doyle's results to dual parameter analysis in order to facilitate comparison with ours for Fe^{II}–EDTA. We find Doyle's data for $Fe(CN)_6^{4-}$ are also well correlated by σ_I and σ_R^+, with $\rho = 4.51$ and $\lambda = 0.61$. Thus for $Fe(CN)_6^{4-}$, the reaction constant is significantly larger than for Fe^{II}–EDTA implying that $Fe(CN)_6^{4-}$ is the more selective reductant. If this is the case, transition states formed between diazonium ions and $Fe(CN)_6^{4-}$ would be expected to occur later along the reaction coordinates than those formed with Fe^{II}–EDTA: the observation of a smaller λ value for $Fe(CN)_6^{4-}$ is consistent with this as it implies a relatively large contribution for structure **3c** in the corresponding transition state. The determinant of the selectivity difference between $Fe(CN)_6^{4-}$ and Fe^{II}–EDTA is probably thermodynamic, as reflected by the standard reduction potentials which indicate Fe^{II}–EDTA to be the more powerful reductant.[17] The difference in charge between the two complexes (Fe^{II}–EDTA is dianionic under the conditions of our experiments) would appear not to be as important as it advantages $Fe(CN)_6^{4-}$ in reaction with cationic diazonium ions yet, where comparisons can be made, the absolute rate constant observed for a particular diazonium ion reacting with $Fe(CN)_6^{4-}$ is always slower than that for the same diazonium ion reacting with Fe^{II}–EDTA. A detailed analysis of the work functions for the two different systems is impeded by uncertainties as to transition-state geometries, reaction distances, *etc.*

Comparison of our data on Fe^{II}-EDTA with Doyle's data for decamethylferrocene is less satisfactory than that involving $Fe(CN)_6^{4-}$ (although the same set of five 4-substituted benzenediazonium ions have been studied). The best correlation of Doyle's data using Taft's σ_I and various scales of σ_R involves σ_R^- which we suggest must be an artefact of the data, for no $-M$ substituents are included. [For the substituents actually considered, the set of σ_R^- values differs from the set of $\sigma_{R(BA)}$ values only in that for OMe and from the set of σ_R^0 values only in that for F. Thus a single aberrant point might determine which is the σ_R scale selected statistically to be best. By comparison with dual-parameter correlations of our data, and of Doyle's data for reduction by $Fe(CN)_6^{4-}$, the statistical quality of the correlation of the decamethylferrocene data set, as judged by the *F*-test, is inferior (Table 3)].



Scheme 1

Table 3 Substituent-dependence of the rate constants of reduction of benzenediazonium ions by Fe^{II} complexes

Fe^{II} complex	$E^{\ominus}/V$[a]	Range of magnitude of rate constants/dm^3 mol^{-1} s^{-1}	Hammett ρ value (and σ value used)	Dual parameter results[b]	No. of points[c]	$100R^2$	Confidence level by *F* test	Ref.
$Fe^{II}(EDTA)(aq)$	0.12[d]	10^4–10^5	1.34 (σ^+)	1.74 ($\sigma_I + 0.78\sigma_R^+$)	5 (5)	99.7	>99.0%	This work
$Fe^{II}(CN)_6^{4-}(aq)$	0.36[e]	10^{-1}–10^5	4.7 (σ)	4.51 ($\sigma_I + 0.61\sigma_R^+$)	8 (7)	99.1	>99.9%	16
$(C_5Me_5)_2Fe(CH_3CN)$	−0.23[f]	10^3–10^5	3.3 (σ)	3.82 ($\sigma_I + 1.04\sigma_R^-$)	7 (5)	98.7	>97.5%	16
$Fe^{II}(aq)$	0.77[d]	10^{-2}–10^1	1.0 (σ^+)		6			19

[a] Reduction potentials are quoted relative to the normal hydrogen electrode, with no allowance for solvent variations. [b] Ref. 15. [c] Number of points in original correlation; in parentheses number utilisable for dual parameter treatment. [d] Ref. 8. [e] Ref. 17. [f] Ref. 18.

The standard reduction potentials[17,18] indicate that decamethylferrocene is a stronger reductant than Fe^{II}–EDTA and thus by analogy with previous argument it might be expected that decamethylferrocene should reduce diazonium ions faster and with less selectivity than Fe^{II}–EDTA. However, if the data sets for the reductions of diazonium ions by the two reductants are compared substituent by substituent, the rate constants for Fe^{II}–EDTA are found to be greater than those for decamethylferrocene. The data indicate decamethylferrocene is approximately twice as selective as Fe^{II}–EDTA. Decamethylferrocene is a neutral reductant and diazonium ions are singly charged so no coulombic terms arise between these reactants or the products of their electron tranfer reaction. By contrast, the reaction of dianionic Fe^{II}–EDTA with diazonium ions will be facilitated by the coulombic attraction between the reactants. This might account for the inversion of the order of reactivity expected on the basis of reduction potentials, but why coulombic effects should modulate selectivity is not clear. In view of the uncertainties concerning the solvent difference and the paucity and quality of the data we prefer not to speculate.

Galli[19] proposed a Hammett correlation of data for the reduction of diazonium ions by $\mathrm{Fe^{2+}_{aq}}$. However, the reaction was performed in the presence of Cu^{II} in order to effect Sandmeyer reaction of the aryl radicals produced. Such Sandmeyer reaction would give rise to Cu^{I} which would then complicate the system by introducing another reductant for diazonium ions. We do not believe, therefore, that Galli's results are representative of the reaction intended, and have not analysed these data further.

Experimental

EPR spectra were recorded on a Bruker ESP-300 spectrometer, equipped with X-band Klystron and 100 kHz modulation. Hyperfine splittings were measured directly from the field scan [by determination with an NMR Gaussmeter ER 035 M, calibrated with an aqueous solution of Fremy's salt, a(N) = 1.309 mT;[20] g-values were determined by comparison with that for $^{\bullet}$CHMeOH (g = 2.003 21)[21] obtained from the reaction of $^{\bullet}$OH (from $\mathrm{Ti^{III}/H_2O_2}$) with ethanol. Relative radical concentrations were determined by direct double integration (using the ESP-300): absolute radical concentrations were determined by comparison of doubly integrated signals with those obtained from $^{\bullet}\mathrm{CH_2CMe_2OH}$ (from $\mathrm{Ti^{III}/H_2O_2/Bu^tOH}$) under standard conditions,[22] these having been calibrated with those obtained from a standard solution of vanadyl sulfate.

Flow experiments were conducted by pumping three reagent streams through a mixer which allowed simultaneous mixing *ca.* 35 ms before passage through the cavity of the spectrometer (using a Watson–Marlowe 502 peristaltic pump). The solutions contained, respectively, iron(II) sulfate (together with a twofold molar excess of sequestering agent where appropriate), the arenediazonium ion, and either fumarate anion or iodoacetate anion (at concentrations as given in the text). pH Measurements were made using a Pye–Unicam pH meter PW 9410 with the electrode inserted into the effluent stream. All solutions were deoxygenated both before and during use by purging with oxygen-free nitrogen. The preparation of diazonium tetrafluoroborates has been described previously.[6]

The kinetic simulation program,[23] executed on a DEC VAX computer was kindly provided by Professor D. J. Waddington and Dr. T. M. F. Salmon.

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Appendix

Kinetic analysis to show how the maximum steady-state concentration of radicals formed in a bimolecular reaction varies as a function of reaction conditions.—For a bimolecular reaction $A + B \xrightarrow{k} R^{\bullet}$ $-\mathrm{d}[A]\mathrm{d}t = -[\mathrm{d}B]/\mathrm{d}t = k[A][B]$. Now $[A] = ([A]_0 - [C])$ and $[B] = ([B]_0 - [C])$ where $[A]_0$ and $[B]_0$ are the initial concentrations of A and B and [C] is the amount of either reactant that has reacted after time t. Whence, omitting the brackets for convenience

$$-\mathrm{d}A/\mathrm{d}t = \mathrm{d}C/\mathrm{d}t = k(A_0 - C)(B_0 - C) \qquad (A1)$$

$$\text{Integration gives } \frac{1}{(B_0 - A_0)} \log\left[\frac{(B_0 - C)}{(A_0 - C)}\right] = kt + Q \qquad (A2)$$

where Q is a constant of integration.

$$\text{When } t = 0,\ C = 0 \text{ therefore } Q = \frac{1}{(B_0 - A_0)} \log\frac{B_0}{A_0}$$

whence

$$\frac{A_0(B_0 - C)}{B_0(A_0 - C)} = \exp(B_0 - A_0)kt \qquad (A3)$$

Expansion and rearrangement of eqn. (A3) gives

$$C = \frac{A_0B_0[\exp(B_0 - A_0)kt - 1]}{[B_0\exp(B_0 - A_0)kt - A_0]} \qquad (A4)$$

$$\text{For a steady state in } R^{\bullet}\ 2k_t[R^{\bullet}]^2 = k[A][B] \qquad (A5)$$

Writing the left-hand side of eqn. (A5) as Y and substituting in the right-hand side from eqns. (A1) and (A4) gives

$$Y = \frac{kA_0B_0(B_0 - A_0)^2\exp(B_0 - A_0)kt}{[B_0\exp(B_0 - A_0)kt - A_0]^2} \qquad (A6)$$

Dividing throughout by $\exp(B_0 - A_0)kt$ gives

$$Y = \frac{kA_0B_0(B_0 - A_0)^2}{\{[B_0\exp[(B_0 - A_0)kt/2] - A_0\exp[-(B_0 - A_0)kt/2]\}^2} \qquad (A7)$$

Putting $x = (B_0 - A_0)kt/2$, gives $B_0 = (2x + A_0kt)/kt$ and substitution in eqn. (A7) gives

$$Y = \frac{kA_0(2x/kt)^2(2x + A_0kt)/kt}{\{[(2x + A_0kt)/kt]\exp x - A_0\exp(-x)\}^2}$$

Expansion of the numerator and the exponentials and simplification gives

$$Y = \frac{A_0(2x + A_0kt)}{t\left[\exp x + A_0kt\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right)\right]^2} \qquad (A8)$$

Y increases from zero when A_0 or B_0 is zero, thus the first turning point on Y as a function of x will be a maximum (or a point of inflexion). Writing $[\exp x + A_0kt(1 + \quad + \quad + \cdots)]$ as D, differentiation of eqn. (A8) with respect to x gives

$$\frac{\mathrm{d}Y}{\mathrm{d}x} = \frac{D^2 \times 2A_0/t - A_0(2x + A_0kt)/t \times 2D\left[\exp x + A_0kt\left(\frac{2x}{3!} + \frac{4x^3}{5!} + \cdots\right)\right]}{D^4}$$

$$= \frac{2A_0}{t} \times \frac{\left\{D - (2x + A_0kt)\left[\exp x + A_0kt\left(\frac{2x}{3!} + \frac{4x^3}{5!} + \cdots\right)\right]\right\}}{D^3}$$

$$\text{For a turning point, } \frac{\mathrm{d}Y}{\mathrm{d}x} = 0, \text{ whence}$$

$$\left\{D - (2x + A_0kt)\left[\exp x + A_0kt\left(\frac{2x}{3!} + \frac{4x^3}{5!} + \cdots\right)\right]\right\} = 0 \qquad (A9)$$

Substituting back for D in eqn. (A9) and expansion of exp x gives

$$1 + x + \frac{x^2}{2!} + \frac{x^3}{5!} + \cdots + A_0kt\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right) - (2x + A_0kt)\left[1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots + A_0kt\left(\frac{2x}{3!} + \frac{4x^3}{5!} + \cdots\right)\right] = 0 \qquad \text{(A10)}$$

Simplification of eqn. (A10) and neglecting terms of higher power than x^2 leads to

$$(1.5 + A_0kt)x^2 + \left[\frac{(A_0kt)^2}{3} + A_0kt + 1\right]x - 1 = 0 \qquad \text{(A11)}$$

Whence

$$x = \frac{-\left[\frac{(A_0kt)^2}{3} + A_0kt + 1\right] \pm \left(\left[\frac{(A_0kt)^2}{3} + A_0kt + 1\right]^2 + 4(1.5 + A_0kt)\right)^{\frac{1}{2}}}{2(1.5 + A_0kt)} \qquad \text{(A12)}$$

Eqn. (A12) may be used to evaluate x and hence the value of B_0 which gives the maximum value of Y for a given set of conditions, *i.e.* A_0, k and t. Taking $A_0 = 1.0 \times 10^{-3}$ mol dm^{-3}, $t = 3.0 \times 10^{-2}$ s (the time between the mixing of reactants and their entry into the EPR spectrometer cavity), Table 4 gives the values of x and B_0 characteristic of different k.

It is thus demonstrated that the concentration of B_0 at which the maximum value of Y occurs is equal to that of A_0 for high rate constants and increases as the rate constant diminishes, as observed experimentally (see the text).

From eqn. (A6) it follows that the steady-state concentration of $R^\bullet$ is given by

$$R^\bullet = \left\{\frac{kA_0B_0(B_0 - A_0)^2 \exp(B_0 - A_0)kt}{2 \times 10^9[B_0 \exp(B_0 - A_0)kt - A_0]^2}\right\}^{\frac{1}{2}} \qquad \text{(A13)}$$

where the termination rate constant of $R^\bullet$ is taken as 2×10^9 dm^3 mol^{-1} s^{-1}.

Fig. 8 shows plots of $R^\bullet$ as a function of B_0 for the values of A_0, k and t used above. The experimental behaviour is modelled very satisfactorily.

Table 4

k/dm^3 mol^{-1} s^{-1}	x	$(B_0 - A_0)$/mol dm^3	B_0/mol dm^{-3}
1×10^6	3.02×10^{-3}	2.01×10^{-7}	1.00×10^{-3}
5×10^5	1.10×10^{-2}	1.46×10^{-6}	1.00×10^{-3}
1×10^5	1.32×10^{-1}	8.78×10^{-5}	1.09×10^{-3}
3×10^4	3.36×10^{-1}	7.47×10^{-4}	1.75×10^{-3}
1×10^4	4.62×10^{-1}	3.08×10^{-3}	4.08×10^{-3}

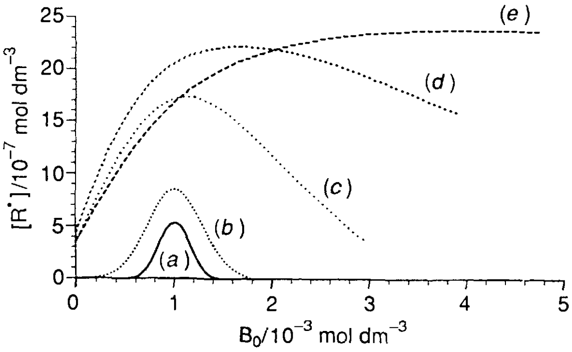

Fig. 8 $R^\bullet$ as a function of B_0[k/dm^3 mol^{-1} s^{-1}: (*a*) 1×10^6; (*b*) 5×10^5; (*c*) 1×10^5; (*d*) 3×10^4; (*e*) 1×10^4]